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DUCLAUX'S METHOD FOR THE ESTIMATION OF "VOLATILE FATTY ACIDS," THE LAWS GOVERNING "VOLATILITY" DEDUCED THEREFROM, AND THEIR APPLICATION TO ANALYSIS, MORE ESPECIALLY TO THAT OF BUTTER.

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(Concluded from p. 198.)

PART II.—RESULTS OBTAINED IN THE PRESENCE OF A SUBSTANCE IN WHICH VOLATILE FATTY ACIDS ARE SOLUBLE AND IMMISCIBLE WITH WATER.

In a method which depends largely on the laws of volatility—the Reichert process—we have conditions which are different to those under which the foregoing experiments were made. In this a mixture of butyric, caproic, and other acids are distilled from an aqueous solution, with which is mixed a quantity of insoluble fatty acids, which Wollny (ANALYST, xiii., 11) has shown dissolve some of the volatile acids. I have already shown (*loc. cit.*) that butyric acid is not held back by insoluble fatty acids, as Wollny supposes.

I have made several practical distillations of butter, with very concordant results, and find that the relation between the volatile acids in the distillate and the volume of the fraction cannot be expressed by a formula of the type $100 - y = \frac{(100 - x)^a}{100^{a-1}} \times k^{-x}$.

The mode of experiment was as follows: 2.5 grammes of butter were saponified by 1 c.c. 50 per cent. soda solution, and 5 c.c. of glycerol or alcohol; if alcohol were used, it was distilled off under reduced pressure, and 55 c.c. water added, but if glycerol, 50 c.c. of water were taken; 20 c.c. dilute sulphuric acid (25 : 1000) was measured into the flask, the fatty acids melted under a reflux condenser, and when this was attained, distillation was proceeded with. Fractions 0–20 c.c. (or 0–22.25) 20–40 c.c., 40–50 c.c., and 50–60 c.c. were collected, then successive portions of 10 c.c. of well-boiled water were added, and distilled till 10 c.c. only took one drop of $\frac{N}{10}$ alkali solution for neutralization; this was taken as the fraction 60–75 c.c., and the sum of the volatile acid in the fractions as the total in the butter.

Up to a certain point they agree well with my butyric acid curve, but at the end of the distillation the want of agreement is very marked.

The following results have been obtained :

Vol. of Distillate. Total = 75 c.c.	Percentage of Acid Distilled.	Acid Distilled $\times 1.072$.	Calc. for Butyric Acid.
20	46.3	49.6	49.4
22.5	50.8	54.4	53.4
40	74.9	80.3	80.7
50	84.4	90.5	90.5
60	91.1	97.6	96.7
75	100.0	107.2	100.0

In the third column the figures are multiplied by 1.072, to show more clearly the agreement with the numbers calculated for butyric acid. The volatile acids of butter appear to distil as a mixture of butyric acid with some other acid volatile towards the end. I have already suggested the presence of lactic acid, but I have been unable to prove its presence. That the apparent divergence from the laws of volatility is due to the presence of the insoluble fatty acids is shown by the numbers obtained on redistilling the distillate from a butter, which Duclaux has shown to distil as a mixture of butyric and caproic acids.

I have shown in the Reichert-Wollny process, when pure butyric acid is used in place of butter, that 96.9 per cent. are distilled when 110 c.c. out of 140 c.c. have passed over ; when 4.4 grammes of well-washed fatty acids were added, 97.2 per cent. were distilled, so that about 97 per cent. of the total butyric acid present should be distilled in the Reichert-Wollny process.

I find four experiments by Wollny (*loc. cit.*), which I have corrected slightly by deducting .22 c.c. for each 110 c.c. of water added and distilled (a figure deduced from my own experiments), and quote four of my own :

		R.-W. Figure.	Total.	Per Cent. Distilled.
Wollny	...	27.94	31.33	89.2
"	...	26.52	30.48	87.0
"	...	27.77	31.51	88.1
"	...	31.07	35.80	86.8
Richmond	...	27.7	32.1	86.3
"	...	29.0	33.4	86.8
"	...	29.1	33.6	86.6
"	...	29.0	33.2	87.4

Thus we see that in the Reichert-Wollny process only about 87 per cent. of the total acid is found in the distillate.

Now, Duclaux has shown that when $\frac{8}{11}$ are distilled, a proportion approximating to the Reichert-Wollny quantities, the composition of the volatile acids in the distillate is approximately 1.8 mols. butyric acid to 1 mol. caproic acid.

I have already shown that 97 per cent. of the butyric acid should distil, so that there should exist in the butter $\frac{1.8}{.97} = 1.856$ mol. butyric acid for 1 mol. caproic acid in the distillate.

To each molecule of caproic acid in the distillate there are 2.8 molecules of volatile acids ; as only 87 per cent. of the acid is found in the distillate, there should be $\frac{2.8}{.87} = 3.218$ molecules of volatile acids in the butter ; of this, it has just been

shown that 1·856 molecules are butyric acid, and therefore 1·362 molecules of caproic acid exists in the butter for each molecule in the distillate. The volatile acids of butter contain 57·7 molecules of butyric acid to 42·3 molecules caproic acid; and from the table given above the following apparent rate of distillation of caproic acid can be deduced:

Vol. of the Distillate. (Total 75 c.c.)	Per Cent. Caproic Acid Distilled.	Calc. for Caproic.	Composition of Vapour.	Composition of Liquid.
20	42·1	73·1	139·5	34·9
22·25	47·3	78·4	124·0	31·0
40	66·9	97·3	82·3	20·6
50	76·1	99·0	62·0	15·5
60	83·5	99·9	65·0	16·4
75	100·0	100·0	—	—

The composition of the vapour is obtained by interpolation, and the composition of the liquid deduced from this by dividing by 4, which, as was shown in Part I., is the ratio between the composition of the liquid and the vapour. From the composition of the liquid and the quantity left in the retort, the quantity of acid dissolved in the liquid can be calculated, and the remainder will be the quantity dissolved by the fatty acids.

Vol. of the Distillate.	Per Cent. Acid in Liquid.	Per Cent. Acid in Fatty Acids.	Composition of Liquid.	Ratio { Per Cent. in Fatty Acids. Composition of Liquid.
20	25·6	32·3	34·9	·9
22·25	21·9	30·8	31·0	1·0
40	10·5	21·6	20·6	1·0
50	5·2	18·7	15·5	1·2
60	3·3	13·2	16·4	·8
75	—	—	—	—

The figures in the fifth column, which are, of course, relative and not absolute, are approximately constant, and when it is considered that they are subject to the following errors—experimental error, error in computation of ratio of butyric acid to caproic acid, errors due to condensation, error due to interference of other acids, *e.g.*, caprylic, and errors in interpolation—the agreement is remarkable.

An extension of Henry's law to express the distribution of a gas between a space and two immiscible liquids shows us that the quantity in the space is an inverse function of the vapour pressure and the solubility in each liquid, and of the bulk of the liquids.

The laws of volatility in the presence of a third body become very complex, and it is practically impossible to obtain any useful information from fractional distillations of butter, unless the whole of the volatile acid be first distilled, and its properties studied in the absence of a second liquid.

To show the nature of the errors thus obtained, Duclaux calculates from his figures that the ratio of the total butyric acid to the total caproic acid in butter is 2 mols. to 1 mol., while from the same figures I calculate the proportion to be 1·36 mols. to 1 mol., and Viollette finds the mean proportion to be 1·65 mols. to 1 mol.

The Viscosimetrical Examination of Butter for Foreign Fats. Dr. Newman Wender. (*Journ. Amer. Chem. Soc.*, xvii., 1895, pp. 719-723.)—It has been well established that there is a definite relation between the chemical composition and the viscosity of liquids, and hence the determination of the rate of transfusion has been found of practical value in the examination of many substances—notably, oils and beer. To the usual apparatus employed for this purpose the author has added the “fluidometer.” (Manufactured by Max Kaehler and Martini, Berlin.) This consists of a U-shaped capillary tube, with the limbs enlarged and divided in such a way that the one holds 10 c.c. and the other 2 c.c. of the liquid. The viscosity is calculated from the time taken by the liquid to flow from the wider limb into the smaller one, which is placed somewhat lower. The apparatus, which is inexpensive, is easily and quickly cleaned.

The researches of Graham (*Liebig Annal.*, 123, 90), confirmed by those of Pribram and Handl and by those of Gartenmeister (*Zeit. Phys. Chem.*, 6, 524), have shown that the viscosity of a liquid increases with the molecular weight. This is evident from the following table :

Fatty Acids.	Pribram and Handl.						Gartenmeister.
	Molecular Weight.	Specific Gravity at 20° C.	Boiling-Point.	Specific Viscosity at 10° C.	Specific Viscosity at 30° C.	Specific Viscosity at 50° C.	Absolute Constant of Friction at 20° C.
Propionic ...	74	0.9929	140.7	70.3	51.5	49.9	−0.1128
Butyric ...	88	0.9580	163.0	110.2	77.4	57.6	−0.1634
Valerianic ...	102	0.9386	184.0	152.4	103.3	71.5	−0.2279
Capronic ...	116	0.9279	199.7	222.2	139.7	97.8	−0.3263
Heptylic ...	130	0.9163	223.0	—	—	—	−0.4440
Octylic ...	144	0.9115	237.0	—	—	—	−0.5860
Nonylic ...	158	0.9053	253.0	—	—	—	−0.8480

Hence margarine with glycerides of a high molecular weight will also have a higher viscosity than butter which contains volatile glycerides in addition. The determinations of Gaselli and Carcano (*Centrbl. Agr. Chem.*, 1894, 838), showed that the molecular weight of pure butter lay between 695 and 715, while that of margarine varied from 780 to 883.

Killing (*Zeit. angew. Chem.*, 1894, 693; *ANALYST*, xx., 66 and 94) confirmed the relationship of the molecular weight to the viscosity in the case of butter and margarine, though the different samples of the latter showed very variable values.

Since, according to Traube (*Berliner Ber.*, 1886, 871), the relation between molecular weight and viscosity is not affected by solvents, the author uses for his “fluidometer” a solution of the melted fat in chloroform, and thus avoids the high temperatures necessary to maintain the fat at the melting-point. The viscosity of the solvent is also to be taken into account. By this method samples of butter from different sources required in the mean 20.04 seconds at 20° C. for efflux. The time required by the solvent was set at 100, and the calculation based on this.

AVERAGE RESULTS.

Viscosity value for pure butter, 344.30. Time, 68.8.

„ „ margarine, 373.20. „ 77.4.

Every degree of temperature above 20° C. decreases the efflux time by 1.45 seconds, but the time the solution of the fat is allowed to stand does not influence the result. A decreasing temperature retards the efflux by an average of 1.43 seconds for every degree.

In the author's opinion, the viscosimetrical examination of butter is as conclusive as any other physical test, but when margarine is present in only a small quantity its detection cannot be effected in this way.

C. A. M.

Test for Distinguishing between Butter and Margarine. (*Pharm. Ztg. Berlin*, through *Seifenfabrikant*, vol. xv., p. 579.)—J. Rolffs, on washing out the sodium butyrate obtained by treating rancid butter with sodium bicarbonate, found that the butter became pale and crumbly in appearance. The same test applied to margarine produced no change, and the presence of this adulterant in butter prevented the alteration signalized in the case of butter alone.

On replacing the sodium compound by potassium carbonate, the following results were obtained, working with 2 to 5 grammes of butter, and employing 20 grammes of water in the washing :

1. The persistent emulsion produced by pure butter is completely dissolved to a clear solution by an equal volume of ether, the line of demarcation between the ethereal and aqueous liquids being sharply defined.

2. With butter and margarine in equal parts an emulsion is obtained, but the lower part of the ethereal solution contains flocculent matter in suspension, and only clarifies by subsidence after prolonged rest.

3. Where the proportion of margarine is raised to three times that of butter, the production of an emulsion is tedious, and requires long-continued agitation. In this case the emulsion is broken up by the addition of half the usual amount of washing water, and the ethereal layer is almost completely filled with suspended matter.

4. On the other hand, neither emulsion nor ethereal solution can be obtained from margarine alone.

The circumstance, therefore, that pure butter, when treated with an alkaline carbonate, will form, with water, an emulsion soluble in ether, whereas margarine gives no such results, its presence in a mixture of the two bodies being revealed by the precipitation of flocculent particles, affords a rapid and reliable means of distinguishing between them, and of detecting adulteration by the last named. C. S.

An Abnormal Butter. J. Samelson. (*Chem. Zeit.*, 1895, xix., 1626.)—A sample of Bavarian butter was recently examined by the author, and gave the following results : Reichert-Meissl number, 21.6 ; Hehner's number, 89.2 ; saponification number, 216.0 ; and iodine number, 42.5. It was therefore returned as adulterated with foreign fat. A thorough investigation followed, and the butter was proved conclusively to be perfectly genuine. Further samples made from the milk of the same cow, and analysed by Soxhlet, gave similar figures.

F. H. L.

Baudouin's Reaction for the Detection of Sesame in Olive-Oil. E. Carlinfanti. (*Selmi*, 1895, v., 49; through *Chem. Zeit. Rep.*, 1895, 215.)—The author finds that the red colour which appears even when the olive-oil examined is pure may be removed by shaking the acid with three times its volume of water; while if only 0.5 per cent. of sesame-oil be present, the colour is not affected by this treatment.

F. H. L.

Lard. M. Mansfield. (*Ztschr. Nahrungsm. Unters. Hygiene*, 1895, ix., 200; through *Chem. Zeit. Rep.*, 1895, 215.)—The author does not believe that commercial lard varies so much in its iodine number as is often reported. He obtains regularly a value of 59 to 62. To test for beef tallow, benzene is the best solvent, pure lard crystallizing therefrom in needles either singly or in bundles, while in the presence of the beef tallow cauliflower-like masses of crystals are obtained. For the detection of further adulteration, the iodine number, crystallizing and solidifying points of the fatty acids may be determined; but for an approximately quantitative idea of the composition of the fat it is necessary, by preparation of the zinc salts and extraction with ether (in which they alone are soluble), to separate the liquid acids. These, as obtained from lard, have an iodine number of 92 and a rotation value of 44 to 45. Vegetable oils subjected to this treatment show a much higher iodine number.

F. H. L.

The Examination of Lard. A. Goske. (*Chem. Zeit.*, 1895, xix., 1043.)—For the detection of tallow in lard, the author still holds that microscopic examination is the surest plan, but the appearance of the crystals obtained from the steam lard and neutral lard of America, is somewhat different from those of ordinary butchers' lards. Not more than 1 gramme of the material is dissolved in 10 c.c. of ether and allowed to crystallize at 12° to 13°C., when pure steam lard will be found to assume the form of sharply defined plates mixed with a few bundles of needle-shaped crystals. If beef-tallow be present, no plates will be visible, the crystals being needles radiating from centres. (They consist of the beef stearin, the pork stearin remaining dissolved.) Butchers' lard also crystallizes in needles, but these are much larger, and more matted together. The addition of either oleomargarine or mutton tallow influences somewhat the appearance of the crystals, but the change can hardly be described.

In testing for the addition of oil, the author has partly given up the use of phospho-molybdic acid, as the indications vary according to the age of the material: he finds, however, that Becchi's silver test in the form recommended by the Italian Commission is quite reliable. Two solutions are prepared—(1) 1 gramme of silver nitrate is dissolved in 200 c.c. of 98 per cent. alcohol, 40 c.c. of ether, and 0.1 gramme of nitric acid added; (2) 15 c.c. of colza-oil dissolved in 100 c.c. of amyl alcohol. For a test, 5 c.c. each of the fat and solution No. 2, and 0.5 c.c. of No. 1 are shaken together and heated in a boiling water-bath for 15 minutes, the coloration being observed over a sheet of white paper. Should the indication appear doubtful, the fat may be pressed gently at 26° to 30°C. and both the oil and the cake examined separately.

F. H. L.

The Detection and Estimation of Glycerin in Beer. M. Molhant. (*Bull. de l'Assoc. Belge des Chim.*, 1895, pp. 17, 18.)—Glycerin is found in beer in amounts varying from 0.1 to 0.5 gramme per 100 c.c. The detection of as much as 0.6 gramme would, therefore, point to the artificial addition of glycerin.

In most of the methods employed the beer is evaporated in vacuo, and the residue taken up with various solvents, but the results are usually too low in consequence of mechanical loss during the manipulation.

With the following modified process of Clausnitzer the author has obtained very satisfactory results: 100 c.c. of the beer are evaporated in a porcelain dish on the water-bath to a syrupy consistence. Three grammes of slaked lime and about 8 grammes of pure calcined silica, or 10 grammes of quartz sand, are added. The mass is well mixed and then completely dried, finishing at 100° to 105° C., after which it is made into a cartridge, and extracted in a Soxhlet with 94 per cent. alcohol for at least six hours. When finished, the alcoholic extract is evaporated to about 50 c.c. and then cooled. The albuminoid bodies, dextrins, etc., are then precipitated by the addition of 30 to 40 c.c. of ether, while the glycerin remains in solution. The liquid is filtered into a weighed flask, and the filter washed with a mixture of alcohol and ether (2 : 3). The filtered liquid is evaporated, and the residue of glycerin dried at 100° to 105° until the weight is constant. The following results were obtained by this method:

Initial Beer.	Glycerin. Grammes.	Anhydrous Glycerin added in Grammes per 100 c.c.	Found. Grammes.
Mons Beer ...	0.21	0.50	0.70
"	0.21	1.00	1.18
Another Sample ...	0.18	0.50	0.68
"	0.18	1.00	1.14
Hal Beer ...	0.39	0.50	0.86
"	0.39	1.00	1.38
Another Sample ...	0.41	0.50	0.90
"	0.41	1.00	1.38

C. A. M.

Estimation of Boric Acid. H. Jay and Dupasquier. (*Comptes Rendus*, cxxi., 1895, pp. 260-262.)—The dried pulverized substance, which must be freed from organic matter, is made very slightly acid with hydrochloric or sulphuric acid, and introduced, together with 25 c.c. to 30 c.c. of methyl alcohol, into a flask fitted with a cork having two apertures. Through one of these passes a vertical tube slightly bent at its lower extremity, which reaches nearly to the bottom of the flask, and is connected with a condenser at the top. The other opening is for a tube which passes to the bottom of a second flask, the outlet of which is connected with the condenser of the first flask. One, two, or three c.c. of a normal solution of potash or soda, free from carbonic acid, are placed in the second flask, the amount being determined by the probable quantity of boric acid, and care being taken to have an excess. The two flasks connected together are then separately heated on the water-bath. The methyl

alcohol removes the boric acid from the first to the second flask, where it is retained by the alkali, while the methyl alcohol passes on through the condenser and back into the first flask, thus making a continuous extraction. The time occupied by the estimation varies, but does not as a rule exceed one and a half hours for a quantity of 300 milligrammes.

The alkaline liquid containing the boric acid is gently warmed to remove methyl alcohol, made up to definite volume, rendered slightly acid with several drops of dilute hydrochloric acid, and very gently warmed to volatilize any traces of carbonic acid. It is then titrated with decinormal potash or soda until turmeric paper indicates neutrality. The indicator "*blue C.L.B.*" is then added, and the titration continued to the neutral point again.

The conditions to be observed are always to work at constant temperatures, and to eliminate methyl alcohol and carbonic acid.

The following samples are given :

					Boric Acid Found. Grammes per Litre.
1 and 2.	Wines taken as typical	...	...	...	0.024
3.	Wine + 0.036 gramme HCl per litre	...	...	...	0.024
4.	" + 0.055 "	"	sodium fluoride	...	0.0255
5.	" + 0.100 "	"	sodium fluosilicate	...	0.0245
6.	" + 0.0062 "	"	boric acid	...	0.0289
7.	{ " + 0.124 "	"	boric acid	...	0.1505
	{ " + 0.110 "	"	ammonium fluoride	...	
8.	{ " + 0.100 "	"	boric acid	...	0.125
	{ " + 0.100 "	"	calcium fluoride	...	
9.	{ " + 0.024 "	"	boric acid	...	0.0495
	{ " + 0.072 "	"	sodium fluoride	...	
10.	{ " + 0.055 "	"	boric acid	...	0.0797
	{ " + 0.072 "	"	hydrochloric acid	...	

It thus appears that fluoric acid causes an increase in weight, but in practice this slight error may be neglected, and the figure obtained attributed to boric acid alone.

Some figures as to the quantity of boric acid in certain animal and vegetable products are also given. Bordeaux and Burgundy wines (1891 and 1892) yielded amounts varying from 0.0105 to 0.022 gramme per litre. Three samples of cider and perry prepared in the laboratory gave 0.011 to 0.017 gramme per litre. The boric acid in four different wines varied from 0.008 to 0.017 gramme per litre. It was not found in a sample of beef-flesh examined by the author.

C. A. M.

Acetic Acid in Vinegar. A. R. Leeds. (*Jour. Amer. Chem. Soc.*, xvii., 1895, 741-744.)—In most cases satisfactory results can be obtained by titrating 5 c.c. of the vinegar diluted to about 50 c.c. with seminormal alkali, using phenol-phthalein as the indicator. With highly-coloured vinegars, however, the end reaction is not sharp. The substitution of litmus-paper or solution as the indicator effects no improvement, lower readings being obtained, and these being lower by a variable amount in different vinegars.

The method of C. Mohr, recommended by Sutton and Wynter Blyth, of adding

an excess of pure calcium carbonate to a known quantity of vinegar and titrating the residual carbonate, failed utterly in the author's hands. To 50 c.c. of vinegar $2\frac{1}{2}$ grammes of finely-powdered calcium carbonate were added, the flask loosely corked, and shaken at intervals for six days. At the end of this time the contents were still acid. In a second experiment the flask was gently heated at intervals—some five or six hours in all. After filtering off the calcium carbonate, the residual acetic acid amounted to nine-tenths per cent. The figure calculated from the residual carbonate corresponded to 3.64 per cent., as against 4.44 per cent. found directly with soda. When a smaller amount of the vinegar (10 c.c.) was treated with an excess of the carbonate under a reflux condenser for two hours, a somewhat better result was obtained, the figure calculated from the residual carbonate being 3.85 per cent., while the liquid contained 0.72 per cent. acetic acid.

The author next tried the distillation process, in which 100 c.c. of 110 c.c. are distilled, and the distillate titrated, or the specific gravity taken. The distillate should contain 80 per cent. of the entire acid present. A trial by this method yielded a distillate with a specific gravity of 1.055 at 15° C., corresponding according to the tables to 4.25 per cent. By titration, the distillate showed (1) 4.23 and (2) 4.24 per cent., as against the correct percentage of 4.43 per cent., which figures correspond to 96 and not 80 per cent. of the total acid.

The process was then varied by distilling 10 c.c. of vinegar with 50 c.c. of water until 2 cc. remained in the retort, when another 50 c.c. of water was added, this being repeated twice more. Even after this long process only 4.39 per cent., or 99 per cent. of the total acid, was obtained. The distillate darkened on adding silver nitrate, and on standing gave a black precipitate.

The distillation was repeated in the same manner, using 10 c.c. of vinegar previously fortified with phosphoric acid. One trial gave 4.507 per cent. acid, another 4.514. The author suggests that the high figure was due to the presence of a little acetate.

Finally, to avoid the influence of the colouring matters, the following method was adopted: 50 c.c. of the vinegar, with 50 c.c. of water and a drop of phenolphthalein, were titrated with decinormal baryta, the latter being added to about 3 c.c. in excess, and this excess subsequently titrated back with decinormal sulphuric acid. The colouring matters subsided readily, either in the cold or upon warming. In one trial the precipitate was filtered off and washed before titrating back with acid, with a result of 4.48 per cent. In another the liquid was made up to 100 c.c., and 25 c.c. pipetted off and titrated; this gave 4.52 per cent. By using turmeric-paper as the indicator, the percentage was found to be 4.43 per cent., which was probably the correct amount.

C. A. M.

The Detection of Martius' Yellow in Macaroni, etc. F. Schaffer. (*Schweiz. Wochensh. Chem. Pharm.*, 1895, xxxiii., 251; through *Chem. Zeit. Rep.*, 1895, 216.)
—When 10-20 grammes of the macaroni or similar substance in small pieces are warmed and shaken with 40 c.c. of 50-60 per cent. alcohol, the presence of colouring matter is shown by the yellowing of the spirit. On the addition of a few drops of

hydrochloric acid, if saffron has been used, the colour is unchanged; if Martius' yellow, it disappears; if metanil yellow, it is changed to red. To determine whether Martius' or naphthol yellow S. has been employed, at least 200 grammes of the substance must be taken, and the alcoholic extract concentrated. Hydrochloric acid then gives with the former a white flocculent precipitate, soluble with a yellow colour in ether. With naphthol yellow S., hydrochloric acid produces no precipitate; but, even in the dilute solution, a flocculent precipitate is formed by caustic soda.

F. H. L.

The Determination of Starch. H. Ost. (*Chem. Zeit.*, 1895, xix, 1501.)—Various contradictory statements having been published by different observers regarding the feasibility of a quantitative estimation of starch, the subject has been carefully reinvestigated. The material employed was potato-starch, which had been repeatedly washed, freed from lumps, and finally air-dried. For the estimation of water, 1 to 5 grammes of the sample are heated in a Liebig's tube in a current of dry hydrogen, the temperature being maintained at 50° to 60° C. for about seven hours, then gradually raised to 120°. Working in this manner the results are very exact, while simple exposure to the air in a watch-glass placed in a drying-oven—the heating being arranged as before—gives figures only 0.1 to 0.3 per cent. too low. If, however, the temperature be raised too quickly, considerable hydrolysis may occur, even at 130° C., whereas a temperature of 150° will effect no injury if the drying be conducted slowly. (The process was checked by subsequent determination of the ash and ultimate analysis, and found perfectly trustworthy.)

For the estimation of the starch itself a number of processes were tried, the one which was found to answer best being that of Sachsse (*Chem. Centralbl.*, 1877, viii., 732), slightly modified. In this modification 3 grammes of the starch are heated with 200 c.c. of water and 20 c.c. of hydrochloric acid, specific gravity 1.125 (= 5.600 grammes of HCl), for two to three hours in a boiling water bath, using the factor 0.925 to calculate the glucose found in the starch. Longer heating gives results too low, and two hours on the water-bath are not sufficient. Slightly higher yields of glucose (89.8 instead of 89.5 per cent.) can be obtained by heating for a much longer period with less starch and acid, but there is no advantage to be gained by the alteration. Oxalic acid gives no better results. Dextrin may be determined in the same manner; also maltose, if 1 gramme of the latter be heated for five hours with 100 c.c. of 1 to 2 per cent. hydrochloric acid as before.

Of the optical methods of examination, the following modification of Effront's process (*Monit. Scient.*, 1887, 538) gives constant results, and may be used, therefore, for approximate commercial work; there is, however, decomposition of the starch: 2.5 grammes of the sample are rubbed down in a mortar, with 10 c.c. of hydrochloric acid (specific gravity 1.17) for eight to ten minutes, then diluted to 100 c.c., and polarized. The results varied 0.4°, from $[\alpha]_D = +196.3^\circ$ to 196.7° , for dry starch. The strength of the acid, and the time of rubbing together, must not be departed from.

By heating 2 to 3 grammes of the starch with 80 to 90 c.c. of plain water for three to five hours in a Lintner's flask to a pressure of 2 to 3 atmospheres, the use of the acid can be avoided. Solutions so obtained have no effect on Fehling's solution,

and, though somewhat opalescent, polarize well (+196.5 to 197.0). In cases where the energetic action of this process caused the solution to have a slight reducing action this was found to be without influence on the rotatory power. Baudry's salicylic acid method was not investigated.

The remainder of the paper, which is exceedingly interesting and of great length, is devoted to an examination of the products of the transformation of starch by diastase, glycerol, etc. The author comes to the conclusion that Lintner's isomaltose has no real existence, and that the series of bodies recently obtained by Zulkowski on heating starch with glycerol are not true dextrins, but compounds of those bodies with glycerol. He also expresses grave doubts as to the validity of the amyloin theory of Brown and Morris.

F. H. L.

On the Action of Alkaline Copper Solutions on Sugars. J. Kjeldahl. (*Meddelelser fra Carlsberg Lab.*, V., 1895, pp. 1-63.)—It has often been noticed that in estimating sugar by the Soxhlet method, or one of its modifications, there has been but little agreement in the results obtained by different chemists. The author considers that much of this difference is due to the influence exercised by the atmospheric oxygen in increasing the weight of the cuprous oxide while heating the liquid. The action of oxygen during filtration need not be feared. That the manner in which the air has access to the vessel during heating influences the result was clearly shown by the following experiment :

I. 30 c.c. of Fehling's solution were added to a sugar solution containing 60 mg. of glucose in a 150 c.c. flask, and the liquid made up to 100 c.c. The stopper of the flask was fitted with two tubes, one reaching nearly to the bottom. Hydrogen was passed through for some minutes, the flask warmed on the water-bath, and the deposit filtered after twenty minutes through asbestos, dried, reduced in hydrogen, and weighed. Parallel determinations were also made in which the air had free access: II., in flask with narrow neck (100 c.c.); III., in conical flask, similar to that used in I.; IV., in a beaker; V., in a deep basin; VI., in a very shallow basin. The amount of surface in contact with the air is given in the first column below :

			Free Surface, square cm.	Copper found, mg.	Difference, mg.
I.	...	...	0	126.3	
II.	...	...	2	126.0	0.3
III.	...	...	17	123.9	2.4
IV.	...	...	21	121.5	4.8
V.	...	...	65	114.8	11.5
VI.	...	...	186	106.6	19.7

Concordant results were obtained on repetition, and it made no difference whether the liquid were cooled or not before filtration. It thus appears that to obtain satisfactory results the heating should be done in a current of hydrogen.

Experiments on glucose proved that within certain limits the proportion of caustic soda in the Fehling's solution had but little influence on the result. Thus, taking half or double the quantity only, showed a difference of 1 per cent. The

influence of the tartrate was somewhat greater, as doubling this constituent decreased the amount of reduced copper by 4 per cent. In the case of maltose and lactose the amount of soda used was of much greater importance.

However pure its constituents, Fehling's solution undergoes a slight reduction on prolonged heating, this being most marked in concentrated solutions. Thus, on heating for twenty minutes on the water-bath in a current of hydrogen, the following results were obtained :

100 c.c. Fehling's solution in 100 c.c.	...	11.3 mg. copper.
75 " " "	...	10.2 "
50 " " "	...	5.2 "
30 " " "	...	2.7 "
15 " " "	...	0.2 "

On prolonged warming this spontaneous reduction was greatly increased. Thus, 30 c.c. of Fehling's solution in 100 c.c., kept on a boiling water-bath for six hours, yielded 57 mg. of copper.

With regard to the length of time of boiling, the author found that after twenty minutes the weight of the copper increased only very slowly, and therefore fixed on that time as the limit for exposing to boiling water.

It will usually be found most suitable to use 30 c.c. or 50 c.c. of Fehling's solution in 100 c.c.; only for very small amounts of sugar is it necessary to use 15 c.c. in 100 c.c. From the examination of pure specimens of different kinds of sugar the author has constructed the following tables :*

15 C.C. FEHLING'S SOLUTION.

Copper, mg.	Glucose.	Fructose.	Invert Sugar.	Galactose.	Lactose, $C_{12}H_{22}O_{11} + H_2O$.	Maltose, $C_{12}H_{22}O_{11}$.
5	2.2	2.6	2.5	2.5	3.4	3.7
10	4.4	5.2	5.1	5.0	6.7	7.5
20	9.0	10.4	10.0	10.2	13.6	15.1
30	13.7	15.8	15.0	15.5	20.5	22.8
40	18.6	21.2	20.2	20.9	27.6	30.7
50	23.7	26.7	25.5	26.5	34.9	38.7
60	28.9	32.4	30.9	32.3	42.2	46.9
70	34.3	38.1	36.5	38.3	49.7	55.2
80	40.0	44.0	42.3	44.4	57.5	63.8
90	46.0	50.0	48.3	50.8	65.4	72.4
100	52.3	56.2	54.5	57.5	73.5	81.3
110	58.9	62.5	61.0	64.4	81.8	90.4
120	66.0	69.0	67.8	71.7	90.3	99.8
129	72.9	74.9	74.2	78.7	98.3	108.4

* The intermediate unit values have been omitted, to save space.—*Abst.*

30 C.C. FEHLING'S SOLUTION.

Copper, mg.	Glucose.	Fructose.	Invert Sugar.	Galactose.	Lactose, $C_{12}H_{22}O_{11} + H_2O$.	Maltose, $C_{12}H_{22}O_{11}$.
40	17.8	19.8	19.1	19.8	26.7	30.9
50	22.4	24.9	23.9	25.0	33.6	38.8
60	27.0	30.1	28.8	30.1	40.6	46.8
70	31.8	35.2	33.8	35.4	47.6	54.8
80	36.6	40.5	38.8	40.7	54.6	63.0
90	41.4	45.9	43.9	46.0	61.8	71.2
100	46.4	51.3	49.1	51.5	69.0	79.4
110	51.4	56.8	54.4	57.0	76.4	87.7
120	56.6	62.4	59.8	62.6	83.8	96.1
130	61.8	68.0	65.2	68.3	91.3	104.7
140	67.1	73.7	70.7	74.0	98.9	113.3
150	72.5	79.6	76.3	79.9	106.5	121.9
160	78.0	85.5	82.0	85.8	114.3	130.7
170	83.7	91.5	87.9	91.9	122.2	139.6
180	89.4	97.6	93.8	98.0	130.3	148.6
190	95.3	103.9	99.9	104.3	138.4	157.6
200	101.4	110.2	106.1	110.6	146.7	166.8
210	107.5	116.7	112.4	117.1	155.0	176.1
220	113.9	123.2	118.8	123.8	163.5	185.5
230	120.4	130.0	125.5	130.5	172.2	195.1
240	127.1	136.8	132.2	137.5	181.0	204.7
250	134.1	143.8	139.2	144.5	189.9	214.4
260	141.2	150.9	146.3	151.8	199.0	224.3

50 C.C. FEHLING'S SOLUTION.

Copper, mg.	Glucose.	Fructose.	Invert Sugar.	Galactose.	Lactose, $C_{12}H_{22}O_{11} + H_2O$.	Maltose, $C_{12}H_{22}O_{11}$.
100	44.7	49.1	47.2	49.5	71.4	82.9
110	49.4	54.3	52.2	54.6	78.7	91.3
120	54.1	59.4	57.1	59.8	86.1	99.8
130	58.8	64.6	62.0	65.0	93.5	108.4
140	63.7	69.8	67.0	70.3	100.9	117.0
150	68.5	75.2	72.1	75.6	108.4	125.7
160	73.4	80.5	77.2	81.0	115.9	134.3
170	78.4	85.9	82.4	86.4	123.0	143.0
180	83.4	91.3	87.6	91.9	130.9	151.8
190	88.4	96.8	92.9	97.4	138.5	160.6
200	93.5	102.3	98.2	102.9	146.1	169.4
210	98.7	107.9	103.6	108.5	153.8	178.3
220	103.9	113.5	109.0	114.2	161.5	187.2
230	109.2	119.2	114.5	119.9	169.3	196.2
240	114.5	124.9	120.0	125.7	177.1	205.2
250	119.9	130.7	125.6	131.5	184.9	214.3
260	125.4	136.5	131.2	137.4	192.7	223.3
270	131.0	142.4	137.0	143.3	200.6	232.5
280	136.6	148.3	142.7	149.3	208.6	241.7
290	142.3	154.3	148.6	155.4	216.6	251.0
300	148.0	160.4	154.5	161.5	224.6	260.2
310	153.9	166.6	160.5	167.7	232.7	269.6

Copper, mg.	Glucose.	Fructose.	Invert Sugar.	Galactose.	Lactose, $C_{12}H_{22}O_{11} + H_2O$.	Maltose, $C_{12}H_{22}O_{11}$.
320	159.8	172.8	166.6	174.0	240.8	279.0
330	165.8	179.1	172.7	180.3	249.0	288.4
340	171.9	185.5	179.0	186.8	257.2	297.9
350	178.1	191.9	185.3	193.3	265.4	307.5
360	184.4	198.4	191.7	199.8	273.7	317.0
370	190.8	205.0	198.2	206.5	282.1	326.7
380	197.3	211.7	204.8	213.3	290.5	336.4
390	204.0	218.5	211.5	220.1	299.0	346.2
400	210.7	225.3	218.3	227.1	307.5	356.0
410	217.6	232.3	225.2	234.1	316.0	365.9
420	224.6	239.4	232.3	241.2	324.6	375.8
430	231.8	246.6	239.5	248.5	333.3	385.8
434	234.7	249.5	242.4	251.5	336.8	389.9

To determine the equivalent of acid formed by oxidation of a molecule of sugar, a modification of the iodometric method may be used. This is based on the reactions :



The first reaction is only complete with strong inorganic acids, but by adding an excess of thiosulphate after the potassium iodide and iodate it is soon brought about. On the following day the excess of thiosulphate is titrated with a standard iodine solution. Care must be taken to ensure the absence of carbonic acid before adding the mixture of iodine and thiosulphate.

The author's experiments on glucose and fructose show that, besides formic acid, the oxidation products contain acids of the type $\text{C}_n\text{H}_{2n}\text{O}_{n+1}$, with glycolic, glyceric, trioxobutyric, arabonic, and gluconic acids.

Some experiments on the action of hot sodium hydrate by itself on sugars point to the conclusion that one molecule (180) of glucose or fructose, or $\frac{6}{5}$ molecule of arabinose, give 1.63 acid equivalents; whereas the second group, comprising galactose, maltose, and lactose, give for 180 of sugar an acid equivalent of 1.45.

C. A. M.

The Volumetric Estimation of Sugar by means of Ammoniacal Copper Solution. Z. Peska. (*Rozprawy ceske Akademie*, 1895, v. (II.), No. 19; *nrough Chem. Zeit. Rep.*, 1895, 257.)—In order to avoid the oxidation of the copper suboxide in solution, the author now uses a layer of vaseline, instead of the usual current of hydrogen. Two solutions are prepared: 6.927 grammes of the purest crystallized copper sulphate are dissolved in water, 160 c.c. of 25 per cent. ammonia added, and the whole made up to 500 c.c.; 34.5 grammes of Rochelle salt and 10 grammes of caustic soda are also dissolved and diluted to 500 c.c. For the analysis, a mixture of 50 c.c. of each liquid is heated in a beaker under a layer of vaseline oil 5 mm. thick, to a temperature of 80° C. The sugar solution is run in 1 c.c. at a time for the first test, but on a repetition the whole amount may be added at once. Towards the end of the titration, the temperature must be raised to 85°, and the heating continued for

* $\bar{\text{A}}$ represents a monovalent acid residue.

two minutes when working on either glucose or invert sugar, four minutes for maltose, and six minutes for milk sugar. Dextrin increases the reducing power of the sugar in this solution less than in the one prepared with potash, and as the ammonia has no injurious action, the whole process is both exact and convenient. When saccharose is present, 1 gramme of it has a reducing action equivalent to 0.0026 gramme of invert sugar. In the determination of lactose in milk the albuminoids should be precipitated with lead acetate and the excess of lead removed by sodium sulphate. The following table gives directly the number of milligrammes of each sugar in 100 c.c. of solution.

C.c.'s used.	Glucose.	Invert sugar.	Milk sugar.	Maltose.	C.c.'s used.	Glucose.	Invert sugar.	Milk sugar.	Maltose.
8	997.8	1049.2	—	—	50	163.0	173.2	318.1	360.0
9	889.4	935.1	—	—	51	159.8	169.8	311.9	353.0
10	802.3	844.6	—	—	52	156.8	166.5	306.0	346.3
11	730.7	770.0	—	—	53	153.9	163.4	300.3	339.9
12	670.8	707.6	—	—	54	151.1	160.4	294.8	333.8
13	620.0	654.5	—	—	55	148.4	157.5	289.4	327.9
14	576.3	608.7	—	—	56	145.7	154.7	284.2	322.2
15	538.4	568.9	1033.9	—	57	143.1	152.0	279.3	316.7
16	505.2	534.2	971.4	—	58	140.6	149.4	274.5	311.4
17	475.8	503.3	916.0	1023.0	59	138.2	146.9	269.9	306.3
18	449.7	475.7	866.5	968.8	60	135.9	144.5	265.4	301.3
19	426.3	451.2	822.3	920.3	61	133.7	142.2	261.1	296.4
20	405.2	429.0	782.4	876.3	62	131.5	139.9	256.9	291.6
21	386.0	408.8	746.0	836.4	63	129.4	137.7	252.9	287.0
22	368.7	390.6	713.0	800.0	64	127.4	135.5	249.0	282.6
23	352.8	373.8	682.7	766.5	65	125.4	133.4	245.2	278.3
24	338.2	358.4	654.8	735.8	66	123.5	131.4	241.5	274.1
25	324.8	344.3	629.2	707.5	67	121.7	129.5	237.9	270.0
26	312.4	331.2	605.5	681.3	68	119.9	127.6	234.4	266.1
27	300.9	319.3	583.5	656.8	69	118.2	125.7	231.0	262.3
28	290.3	307.8	563.1	634.1	70	116.5	123.9	227.7	258.6
29	280.3	297.3	544.1	613.0	71	114.9	122.2	224.6	255.0
30	271.1	287.5	526.2	593.2	72	113.3	120.5	221.5	251.5
31	262.4	278.2	509.5	574.5	73	111.8	118.9	218.5	248.1
32	254.2	269.6	493.8	557.1	74	110.3	117.3	215.6	244.8
33	246.6	261.6	479.1	540.8	75	108.8	115.8	212.8	241.6
34	239.3	253.9	465.3	525.3	76	107.4	114.3	210.0	238.4
35	232.6	246.7	452.2	510.7	77	106.0	112.8	207.3	235.3
36	226.1	240.0	439.8	496.8	78	104.6	111.4	204.7	232.3
37	220.0	233.5	428.1	483.7	79	103.3	110.0	202.1	229.4
38	214.3	227.4	417.0	471.3	80	102.0	108.6	199.6	226.6
39	208.8	221.7	406.5	459.5	81	100.8	107.2	—	223.9
40	203.6	216.2	396.5	448.3	82	99.6	105.9	—	221.2
41	198.7	211.0	387.0	437.6	83	—	104.6	—	218.6
42	194.1	206.0	377.8	427.4	84	—	103.4	—	216.0
43	189.7	201.3	369.2	417.7	85	—	102.2	—	213.5
44	185.4	196.7	360.9	408.4	86	—	101.1	—	211.1
45	181.2	192.3	353.0	399.5	87	—	—	—	208.7
46	177.3	188.1	345.4	391.0	88	—	—	—	206.4
47	173.5	184.1	338.1	382.8	89	—	—	—	204.1
48	169.9	180.3	331.2	374.9	90	—	—	—	201.9
49	166.4	176.7	324.5	367.3	91	—	—	—	199.7

Preparation of Sugar Solutions for Polarimetry. **Stift and Petziwal.** (*Oesterr. Zeits. Zuckerind.*, 1895, xxiv., 487; through *Chem. Zeit. Rep.*, 1895, 239.)—The authors point out several objections to the use either of tannin or lead acetate for decolorizing sugar solutions. On the other hand, they strongly advise the employment of Herles' plan, which consists in the employment of lead nitrate. It works well, even in the case of very dark liquids. F. H. L.

The Influence of Lead Acetate on the Determination of Invert Sugar. **Bornträger.** (*D. Zuckerind.*, 1895, xx., 1169; through *Chem. Zeit. Rep.*, 1895, 239.)—The author confirms Gill's old statement that lead acetate causes the amount of sugar as found by Fehling's solution to be too low. The best method of removing the excess of lead salts, especially in the case of wine analysis, is by means of sodium phosphate. The experiments are being continued. F. H. L.

The Chemical Nature of Diastase. **T. B. Osborne.** (*Jour. Amer. Chem. Soc.*, xvii., 1895, pp. 587-603.)—The methods usually employed for the isolation of the enzymes have been to extract the enzyme-containing tissues with water or glycerol, the enzyme being subsequently precipitated in an impure condition from the extract by the addition of alcohol. An attempt was then made to free the enzyme from its attendant impurities by repeated solution in water and re-precipitation with alcohol, the mineral matters being removed by dialysis. According to the author, these processes, the former of which was used by Lintner for the preparation of diastase, are not calculated to yield pure preparations, as the precipitate produced by alcohol contains nearly all the proteid matter present in the extract, as well as a large amount of carbohydrates and salts.

A better method is to first precipitate the proteids, together with the diastase, by saturating the extract with ammonium sulphate, next to remove the globulins by dialysis and, finally, to separate the albumin and proteoses by dialysis in alcohol. The ammonium sulphate does not exercise any injurious action on the diastase. Lintner recommended extraction of the malt with 20 per cent. alcohol, but the author found that although preparations with a high diastatic power could be thus obtained, the method is not so suitable for subsequent precipitation with ammonium sulphate as extraction with water.

Ten kilogrammes of malt were exhausted with water, and the extract saturated with neutral ammonium sulphate. The precipitate was dialyzed in 4 litres of water, until much of the sulphate had been removed, and the precipitated proteid largely dissolved. The insoluble residue, consisting largely of globulin, was then filtered off, and the filtrate saturated with ammonium sulphate. This precipitate was also dialyzed in 1,500 c.c. of water. By this treatment most of the globulin present in the extract was separated, and, after filtration, the clear filtrate was dialyzed into an equal volume of alcohol (specific gravity 0.84). After twenty-four hours precipitate I. had formed and was filtered off. The filtrate was again dialyzed into alcohol of the same strength, and after twenty-four hours precipitate II. was obtained. On dialyzing the filtrate into somewhat stronger alcohol, precipitate III. separated out, while precipitate IV. was

obtained in a similar manner. The filtrate from this yielded precipitate V. on the addition a large quantity of absolute alcohol. In this way all the proteid in the extract was separated. The approximate weights of the precipitates were: I., 13; II., 8; III., 6; IV., 5; and V., 3 grammes.

Precipitate I. was largely insoluble in water, and, after filtration and dialysis of the filtrate, yielded a preparation with a diastatic power of 30 by Lintner's test. It was found to consist largely of proteose. The portion insoluble in water consisted of globulin-like substances.

Precipitate II. was treated with water, and the solution dialyzed for several days in water, a quantity of absolute alcohol being finally added, which precipitated the proteid. The dried preparation was almost completely soluble in water, and the solution on heating became turbid at 60° C., and flocculent at 66° C. It contained a slight amount of insoluble matter, some albumin, and much proteose. Its diastatic power was 75. The part insoluble in water was similar in composition to the corresponding residue in I.

Precipitate II. contained less globulin and proportionately more albumin and proteose than I., and had, therefore, a higher diastatic power.

Precipitate III. was treated in the same way as II. The resulting precipitate, which was almost completely soluble in water, yielded a solution which became turbid at 55° and flocculent at 60°. The diastatic power of the preparation was 122. The insoluble residue was considered to be impure globulin.

Precipitate IV., treated as in the other cases, yielded a preparation which dissolved to a nearly clear solution in water. The filtered solution became turbid at 50° and coagulated at 56°. This preparation had a diastatic power of 600. At 20° it was able to produce from soluble starch 2,000 times its weight of maltose. Its composition, neglecting ash, was: Carbon, 52.50; hydrogen, 6.72; nitrogen, 16.10; sulphur, 1.90; oxygen, 22.78. This diastase had therefore six times the diastatic power of the most active preparation made by Lintner; which, since it only contained 10.42 per cent. nitrogen, led him to conclude that diastase was not a true proteid.

Precipitate V. dissolved completely on treatment with water. It was precipitated and washed with absolute alcohol, and yielded a preparation with a diastatic power of 60. Its aqueous solution became turbid at 50° and flocculent at 58°. It consisted chiefly of proteose.

It thus appears that in malt extract there is a globulin, an albumin, and at least one (more probably two) forms of proteose. The amount of proteose diminished from precipitate I. to IV., which contained the least, while V. was mainly proteose. The globulin is rendered insoluble more readily than the albumin, and may thus be separated.

The author's general conclusion is that diastase is most closely related to the albumin, this being shown by the behaviour and composition of the preparation obtained from precipitate IV. The amount of coagulable albumin in this preparation was found to be 53.2 per cent. of the dried substance.

W. J. S. & C. A. M.

NOTE BY THE ABSTRACTORS.—We are able to confirm the statement that the

activity of malt diastase is not affected by precipitation with ammonium sulphate. Acting upon a hint given in the original paper, we find that the diastase is completely precipitated from aqueous malt extract on saturation with magnesium sulphate, without its activity being diminished. The precipitate obtained with the latter salt is infinitely smaller in bulk than that obtained by means of the former.

The Detection of Water in Acetone. H. Schweitzer and E. E. Lungwitz. (*Chem. Zeit.*, 1895, xix., 1384.)—By shaking together equal volumes of acetone and petroleum ether (b. p. 40 to 60° C.) the presence of a small quantity of water in the former is shown by the separation of the liquid into two layers. With dry acetone no such separation takes place. The reaction is only qualitative. By the employment of a heavier spirit (b. p. 80 to 100° C.), followed by distillation, the authors are attempting to work out a process for commercial use. F. H. L.

Antipyrine and the Thalleioquin Reaction. J. Ducommun. (*Schweiz. Wochenschr. Chem. Pharm.*, 1895, xxxiii., 242; through *Chem. Zeit. Rep.*, 1895, 214.)—One part of antipyrine in the presence of twenty parts of quinine prevents the appearance of the well-known green colour of this test, producing in its stead a fine red. Urea stops the production of either colour, while the salts of morphine, pilocarpine, cocaine, strychnine, codeine and atropine, chloral hydrate, and phenol, etc., in 1 per cent. solutions are without influence on the green tint. F. H. L.

The Estimation of Iodine in Organic Substances of the Fatty Series. M. C. Schuyten. (*Chem. Zeit.*, 1895, xix., 1143.)—A weighed amount of the substance, chosen so as to contain 0.03 to 0.05 gramme of iodine, is put into a glass tube holding about 15 c.c., then some freshly-melted and finely-powdered potassium bichromate mixed with it by agitation, and finally a layer 5 to 6 c.m. thick of bichromate. The end of the tube is drawn out and bent. By gentle heating, the iodine is then sublimed into the narrow part of the tube, which is kept cold by a wet cloth. When all has come off, and the molten substance is perfectly clear, the tube is cut off, the iodine washed out with potassium iodide solution, and titrated in the usual manner. It may also be weighed direct by placing the cut-off tube in connection with a tube containing calcium chloride and some lumps of caustic soda till all moisture has disappeared. The results quoted by the author are satisfactory. F. H. L.

Ionone and Irone. F. Tiemann and P. Krüger. (*Ber.*, 1895, xxviii., 1754.)—The authors describe several condensation products of these ketones, by means of which their presence and purity may be established. The semicarbazides of both substances are produced by the action of semicarbazide sulphate on the ketones in glacial acetic acid solution, the ionone compound melting at 109° to 110° C. From a cold solution of parabromophenylhydrazine in acetic acid of such a strength that it will bear the addition of an equal or double volume of water without crystallizing,

ionone - parabromophenylhydrazone may be prepared as a white or light-yellow crystalline precipitate. If the ionone is pure, the hydrazone appears in very characteristic glittering leaf-like crystals, which, when dry, soften at 134° , and melt to a clear oil at 140° to 145° C., crystallizing again on cooling. Impure preparations may be recrystallized from hot methyl alcohol to which a little water has been added. Mineral acids gradually convert the hydrazone into the original ionone, as may be detected by the violet-like odour.

The corresponding compound of irone may be prepared in a similar manner; it crystallizes in groups of needles, which soften at 156° , and melt at 168° to 170° C. When water is added gradually to a cold or slightly warm acetic acid solution of the two hydrazones, the irone compound is first precipitated, and the ketones may be separated in this manner. The above-described reactions take place quantitatively, and they can be employed for the estimation of either perfume. F. H. L.

Volumetric Estimation of Arsenic in Iron and Steel. A. Mignot. (*Rev. Chim. anal. appliq.*, 1895, iii., 101; through *Chem. Zeit. Rep.*, 1895, 164.)—Ten grammes of the metal are dissolved in nitric acid and evaporated, and the residue ignited to decompose the nitrates; the powdered mass is treated with concentrated hydrochloric acid in the cold for an hour. The whole, solution and residue, is introduced into a long-necked, 500 c.c. flask, made up to 300 c.c. with strong hydrochloric acid, and 50 c.c. of saturated ferrous chloride solution added. This flask is connected, through a condenser, with a small flask, into which the leading-tube only just enters, while a second tube, starting from the bottom of the latter, is bent so as to dip into some water contained in a beaker. The distillation is continued till only 100 c.c. are left in the first flask, care being taken, by removing periodically the beaker, that the distillation does not become sufficiently violent to cause any of the liquid to boil over. The distillate is made up to 500 c.c., precipitated with sulphuretted hydrogen, and the sulphide filtered off, washed and dissolved in 20 c.c. of (1:3) ammonia. It is again precipitated with 20 c.c. of acetic acid of $\frac{5}{4}$ times the equivalent strength, iodine solution added, and the excess titrated with thiosulphate. The iodine is standardized on an arsenic solution precipitated, etc., as above described. It is stated that this process will estimate 0.005 grammes of arsenic. (Compare Fresenius, *Quant. Anal.*, vol. ii., 6th (German) edition, p. 558 *et seq.*)

F. H. L.

The Separation of Arsenic from other Elements by means of Methyl Alcohol and Hydrochloric Acid. C. Friedheim and P. Michaelis. (*Ber.*, 1895, xxviii., 1414.)—Fischer's method for the estimation of arsenic by distillation with ferrous chloride and hydrochloric acid is inconvenient in many cases, as the presence of the ferric chloride resulting from the operation complicates the determination of other substances in the liquid after the arsenic has been removed. Methyl alcohol is free from this disadvantage, as it adds nothing to the bodies under treatment beyond a small amount of carbon.

The liquid is introduced into a 250 c.c. flask fitted with a stoppered dropping

funnel, and connected with a condenser and a flask of 750 c.c. capacity, in which 20 c.c. of strong nitric acid are placed. To this flask is connected a set of potash bulbs filled with water, all the joints being preferably ground in. To the liquid are added 50 c.c. of methyl alcohol, which must be kept as dry as possible, and if much water has been employed in introducing the substance into the flask, most of this should be first distilled off. A rapid stream of dry hydrochloric acid gas is introduced through the funnel, the flask being kept cold, and care being exercised that the liquid is not drawn back. When completely saturated, the stream of gas is slackened, a water-bath attached, and the whole distilled. According to the amount of arsenic and water present, the operation is repeated a second or third time, more alcohol being added if required.

The distillate, etc., is washed out into a large porcelain basin, 20 to 30 c.c. of strong nitric acid added—the basin being covered over to avoid loss during the evolution of gas—and then the liquid evaporated down to 100 c.c. A second equal amount of nitric acid is employed, and the whole evaporated to dryness, taken up in water, and precipitated with magnesia mixture. The authors have satisfactorily effected the separation of arsenic from vanadium, tungsten, and molybdenum by this process.

F. H. L.

The Preparation of Pure Zinc. F. Mylius and O. Fromm. (*Zeits. Anorgan. Chem.*, 1895, ix., 144; through *Chem. Zeit. Rep.*, 1895, 198.)—By the term “pure” zinc the authors understand a metal spectroscopically as well as chemically pure, whereas the purest commercial zinc usually contains iron, lead, and cadmium in amounts of at least 1.4, 5, and 16 parts per 100,000 respectively. The latter two impurities are best detected and estimated by fractional precipitation with ammonium sulphide in an ammoniacal nitrate solution, the reagent being added until the precipitate falls of a pure white colour. For the preparation of the pure metal fractional crystallization of commercial zinc is useless, but by boiling the nitrate solution freed from other metals as indicated and igniting the precipitate, pure zinc oxide may be obtained. By electrolyzing a solution of the sulphate, using zinc oxide to neutralize the acid set free, a product is obtained contaminated with platinum from the anode. The purest metal may be prepared by the repeated electrolysis of a basic sulphate solution, the zinc being finally sublimed *in vacuo*, when it will be found not to contain more than 1 per 100,000 parts of impurity.

F. H. L.

The Volumetric Determination of Zinc, and a New Indicator for Ferrocyanide. G. C. Stone. (*Journ. Amer. Chem. Soc.*, 1895, xvii., 473-477.)—In titrating zinc with ferrocyanide, the metals of the iron group must first be removed. Since no rapid and accurate method for separating manganese and zinc is published, the author proposes titrating them together, determining the manganese in a separate portion by titration with permanganate, and taking the zinc by difference. The best indicator for ferrocyanide when used with manganese was found to be cobalt nitrate. A drop of a quite dilute solution is placed on a tile beside a drop of the solution to

be tested, just touching but not mixing with it. The end reaction is shown by an immediate faint green line at the junction of the drops.

The best strength for the ferrocyanide solution is about 30 grammes per litre. It is standardized by titrating solutions containing known amounts of zinc or manganese, making slightly acid with HCl, and keeping the solution at about the volume used in the analysis. The amount of ferrocyanide necessary to give a reaction with cobalt in this volume of acidified water must also be determined, and the result deducted for each titration.

The permanganate solution is standardized in the usual way with iron, the result being multiplied by 0.294646. It contains 1.99 grammes of crystallized potassium permanganate per litre, 1 c.c. being equivalent to 0.001 gramme of manganese. The ore is dissolved in HCl with the addition of KClO_3 as an oxidizer, and care must be taken to have sufficient acid to keep all the manganese in solution.

Lead alone need not be separated; copper can be precipitated by lead; or lead and copper can both be precipitated by aluminium. Cadmium should be precipitated by H_2S , and the filtrate oxidized. Iron and aluminium are best separated by barium carbonate, but the latter must be free from alkaline carbonates and hydroxides, barium hydroxide and ammonium salts. A salt sufficiently pure for the purpose may be obtained by suspending the ordinary "pure" carbonate (first proved free from ammonium salts) in warm water for several hours with 2 or 3 per cent. of its weight of barium chloride.

The well-oxidized solution of the ore is put into a 500 c.c. flask, and barium carbonate suspended in water added until the precipitate coagulates. The whole is then poured into a beaker, well mixed, allowed to settle, and the clear liquid decanted through a dry filter. Portions of 50, 100, or 200 c.c. of the filtrate are used for each titration. One portion, which should contain between 0.01 and 0.04 gramme of manganese, is diluted to 200 c.c., heated nearly to boiling in a porcelain dish, and titrated rapidly with permanganate with vigorous stirring.

In a second portion made *slightly* acid with hydrochloric acid, the zinc and manganese are titrated together in the cold with ferrocyanide; the dark colour of the precipitate suddenly changes to light yellowish green shortly before the end of the reaction. It is not necessary to test with the cobalt solution until 1 or 2 c.c. of the ferrocyanide solution have been added after the lightening of the precipitate.

To show the calculation of the results, the following example is given: 1 c.c. of the ferrocyanide solution equalled 0.00606 gramme of zinc, or 0.00384 of manganese; 1 c.c. of the permanganate equalled 0.001 gramme of manganese. $2\frac{1}{2}$ grammes of the ore were dissolved, and the iron precipitated and filtered out. 50 c.c. of the solution were diluted, heated, and titrated with permanganate, requiring 18.45 c.c. = 7.38 per cent. of manganese. 100 c.c. titrated with ferrocyanide required 27.85 c.c., of which 9.61 c.c. would be used by the manganese present. Deducting this, 18.24 c.c. was left for the zinc, equal to 0.11053 gramme, or 22.11 per cent. The amounts of zinc and manganese as determined gravimetrically were 22.05 and 7.58 per cent. respectively. The other results tabulated are equally satisfactory.

C. A. M.

An Improved Burette. F. Oettel. (*Chem. Zeit.*, 1895, xix., 1384.)—The upper end of an ordinary Mohr's burette is expanded to form a funnel of about 30 mm. diameter, which may be closed by a sphere of glass to prevent entry of dust. So improved, the burette may be slung from this funnel, and tilted out of the vertical when titrating hot solutions. The graduations are not obscured by the ordinary clamp, and filling is much facilitated.

F. H. L.

REVIEWS.

THE SCIENCE AND ART OF BREAD-MAKING. By WILLIAM JAGO, F.I.C. (London: Simpkin, Marshall, Hamilton and Co.) Price 15s. net.

It is most difficult to form an idea for what class of reader this bulky volume has been compiled, whether for the scientist or for the baker and miller. If for the former, it contains a great deal of matter altogether unnecessary, and in many instances of doubtful value; if for the latter, it is highly questionable if there are many millers or bakers in the country who will be any the wiser for reading it.

That part of the work which relates more strictly to bread making and baking, and which contains much original work carried out by the author, is, though diffuse and often smacking of objectionable self-advertisement, a valuable contribution to the knowledge on the subject. The work of C. O'Sullivan, Horace Brown, and other investigators on the carbohydrates is fairly and clearly given; so also are the modern views as to the nature of fermentation. Analytical processes for the examination of flours and bread are also given in great detail and with accuracy.

The scientific introductory chapters, on the other hand, are open to much criticism, and contain very numerous statements and expressions to which exception may be taken. The first three chapters, which travel over the whole region of chemistry and physics, bristle with inaccuracies and slipshod writing. We quote a few of these: "Many, if not most, liquids mix readily with water in all proportions"; "Most solid bodies dissolve in water"; "Phosphorus occurs ordinarily in sticks"; "Calcium is scarcely known in the free state"; "Calcium hydrate occurs as a dry white powder"; "It has been proposed to define organic chemistry as the chemistry of carbon compounds." This definition, however, does not please the author, so he defines organic chemistry "as that branch of the science which treats of the composition and properties of those compounds whose usual source is either animal or vegetable." Under this definition, therefore, all such compounds as zinc-ethyl would be removed from the realm of organic chemistry! "The temperature of the boiling-points increases," etc.; "The alcohols are hydrates of the organic radicals." Mannite is stated to be the mother substance from which all the other carbohydrates are supposed to be derived—a statement which is only true for some of the hexoses. Margaric acid is still quoted as a constituent of natural fats; oleic acid is stated to be the product of oxidation of an alcohol; "Oleates of glycerin constitute the oils"; "The separation of fats into glycerin and the fatty acids may be effected by forcing a current of steam through the melted fat"; "But little is understood of the constitution of the alkaloids." And so on *ad infinitum*.

The chapter on the constitution of the carbohydrates is a long way behind the present state of science. The author, for instance, says that the glucoses (dextrose, lævulose, and galactose being the only three representatives referred to by him) are the aldehydes of mannite. It is now well known that lævulose is not an aldehyde, but a ketose. Vegetable ivory is stated to be nearly pure cellulose; it contains, however, a large quantity of mannan, the parent substance of mannose. Lævulose is stated to be not crystallizable, although crystallized lævulose has been for some years an article of commerce. An analysis by the author of the fat of the germ of wheat shows 26.93 per cent. of glycerin, and the analytical results sum up to 100, although the glycerin and fatty acids are given as such without subtraction of water. This percentage of glycerin cannot be accepted as even an approximation to the truth.

A most objectionable feature of the book, from a professional point of view, is the advertising part, both without and within the body of the work. There are forty-two pages of advertisements, exactly one-third of which contain the name of the author, either in advertising reports given to makers of all sorts of articles, or in direct advertisements on behalf of Mr. Jago. A long list of the names and addresses of millers whose flours are described in the body of this work is also given, and copies of certificate-forms, with Mr. Jago's name and qualifications, are contained in the text of the book itself. This is hardly consonant with the present standard of professional ethics.

Altogether the work is of most unequal merit, for the sound information contained in the book is in danger of being stultified by its numerous inaccuracies.

O. H.

POISONS, THEIR EFFECTS AND DETECTION. By A. WYNTER BLYTH. (London: C. Griffin and Co. Price 21s.)

This work is undoubtedly the most complete treatise on toxicology in our language, and should be in the library of every analyst and teacher interested in the subject. It begins with a brief but very interesting historical sketch, carrying us in twelve pages from Greek myths, through ancient Egyptian and Hebrew lore, down to the Italian poisoners of the seventeenth century.

This is followed by some pages of an equally interesting account of the improvements introduced from time to time into our methods for the detection of poisons. These chapters will be highly appreciated by all earnest students who, not having time or opportunity to study the original memoirs, have yet the wish to possess some knowledge on these subjects. We heartily thank the author for the trouble he has taken to bring these facts to our knowledge in so compendious a form.

Next follow chapters common to all works on the subject—the definition of a poison and the classification of poisons; but even on these the author has succeeded in impressing his own individuality. The author does not, however, follow the beaten track for long, but next favours us with several chapters on the statistics of poisoning in England, Germany, and France, and a very valuable account on “the connection between toxic action and chemical composition.” In these chapters the author breaks practically new ground, as far as general works on toxicology are concerned, and all students will be indebted to him for so clearly and concisely bringing together

the scattered information on this important subject. With a series of chapters on the identification of poisons by experiments on animals, a general method in searching for poisons, the use of the spectroscope, and the examination of blood-stains, what we may term the introductory part of the work comes to an end. It will be seen in how unusually comprehensive and complete a manner this portion of the subject has been treated, and our gratitude is due to the author for the able way in which he has carried out his plan.

Where so much is given it may appear ungracious to ask for more, but we cannot help expressing a wish that in future editions the author will favour us with some general remarks on the following subjects, which are of great importance to the practical toxicologist, but are greatly neglected in all works on toxicology—namely, some account of the rate of absorption of poisons in various forms and in various ways, together with their distribution during absorption in the various organs and tissues of the body; the rate at which poisons are either eliminated from, or destroyed within, the system, and the relative proportions in which they are found in the various organs and tissues, etc., in the course of such elimination. We know no one who could better give us information on these subjects than the gifted author of the work before us. It is impossible, in the space at our command, to give anything like a full account of the contents of this handsome volume of over 700 pages, and we must content ourselves with a few general remarks regarding the remainder of the volume.

In the first place, the author has departed somewhat from the usual order in treating the various poisons. This departure is based on the author's general method for the detection of poisons, and is fully justified thereby. Ample information is generally given regarding the physiological and chemical characters of the various poisons treated of, together with the best methods for their separation and identification. This part of the work is very complete; in fact, the details given are sometimes too ample, and render the work, occasionally, rather difficult as a practical guide. We have found the information given generally reliable and fully up to date. In some places, however, the author adopts what we cannot but call the inconvenient plan of referring the reader to other works of his for further information, instead of, as ought to have been done, giving the information in the present volume. Some readers may also regret the almost total absence of records of important trials, which render Taylor's great work so interesting and instructive.

In conclusion, we can heartily recommend the work to all our readers, and congratulate the author on the extremely able and original manner in which he has accomplished a task of no common difficulty.

A. D.

AIR, WATER, AND DISINFECTANTS. By C. M. AIKMAN, M.A., D.Sc., F.R.S.E. (Society for Promoting Christian Knowledge.) Price 1s.

This handy little book, which forms one of a series of "Manuals of Health" published by the above society, contains much useful information put into exceedingly readable form. The instruction imparted is trustworthy and well up to date. The work cannot fail to be of considerable use to the class of readers to which it is addressed.